hydrocarbons[28] making it difficult to resolve the different signals except at low temperatures.

The flexibility of the dimethylgallium(III) hydroxide tetramer is much greater than that of the dimethylgold(III) hydroxide tetramer. The gold compound still shows two equal-intensity methyl proton resonances up to above 100°, while the analogous dimethylgallium hydroxide shows only a single methyl proton resonance at temperatures as low as −81°.

**Acknowledgment.**—The authors wish to express their appreciation to Dr. S. J. Harris for the measurements of the acid dissociation constants of $(CH_3)_2Ga_{aq}^+$ and for helpful discussions. Thanks are also due to Mr. S. H. Sage for help in preparing the manuscript.

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# Raman and Infrared Spectra of Isosteric Diammine and Dimethyl Complexes of Heavy Metals. Normal-Coordinate Analysis of $(X_3Y)_2Z$ Ions and Molecules[1]

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*Received March 22, 1968*

Raman and infrared spectra have been measured for $(H_3N)_2Ag^+$ and $(H_3N)_2Hg^{2+}$. For comparison with the aqueous solution spectra, the Raman spectrum of aqueous ammonia was also studied. Although the metal–nitrogen skeletal stretching vibrations give intense Raman scattering, the lines are very broad. Also in contrast to the analogous scattering by the isoelectronic "methido" complexes, this Raman scattering measured with aqueous solutions is only very weakly polarized. This is probably a result of the strong hydrogen bonding between the ammine groups and the solvent cage. A normal-coordinate analysis of these two ammine complexes and the isostructural dimethyl derivatives $(H_3C)_2Cd$, $(H_3C)_2Sn^{2+}$, $(H_3C)_2Hg$, $(H_3C)_2Tl^+$, and $(H_3C)_2Pb^{2+}$ has been made, including all of the ligand atoms, in order to describe the nature of the normal modes and to permit comparisons along isoelectronic sequences. Variations in the force constants are discussed. In addition, calculations were made for the isostructural $(F_3C)_2Hg$ in an attempt to ascertain the effect on the carbon–mercury bond of altering the effective electronegativity of the carbon atom.

## Introduction

During the past few years, there have been many reports of syntheses of compounds containing organometallic moieties such as $(H_3C)_2In^{III}$, $(H_3C)_2Tl^{III}$, $(H_3C)_2Sn^{IV}$, and $(H_3C)_2Pb^{IV}$. Much of this work has been reviewed recently.[3–5]

In many instances, infrared and to a lesser extent Raman spectra have been used to ascertain the structure of the organometallic moiety and consequently often that of the entire complex. To assist in such work, we decided to carry out a vibrational analysis of several of these organometallic moieties together with two isoelectronic and isostructural ammine complexes for comparison. In addition, because the methyl derivatives generally yield much better Raman and infrared spectra than metal ammines, they are of value in answering some, as yet, unresolved questions about the skeletal vibrations of heavy-metal ammine complexes.

Raman and infrared spectra have been obtained previously for several "methido" complexes of metals, *i.e.*, the methyl derivatives. The dimethyl derivatives which have been studied and which are isoelectronic and isostructural with well-known metal ammine complexes include $(CH_3)_2Cd$ for which Raman (R)[6] and infrared (ir)[7] spectra have been reported; $(H_3C)_2Hg$ (R),[8] (ir);[8,9] $(H_3C)_2Tl^+$ (R);[10] $[(H_3C)_2Sn]^{2+}$ (R, ir);[11] and $[(H_3C)_2Pb]^{2+}$ (R).[12] An additional molecule of this same structural type for which both Raman and infrared data have been reported is $(F_3C)_2Hg$.[13]

The good quality of the spectra of these "organometallic" complexes even with cations such as $(CH_3)_2Pb^{2+}$ for which spectra must be obtained with crystals or aqueous solutions is a consequence of the absence of strong hydrogen bonding which broadens and distorts the spectra of metal ammines.

The infrared spectra of metal ammine complexes have been investigated by many authors,[14] and normal-coordinate calculations have been carried out for several transition metal hexaammines,[14,15] $[(H_3N)_2Hg]^{2+}$,[14] tetraammineplatinum(II),[16] and some diammineplatinum(II) complexes.[17]

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(2) Author to whom inquiries should be addressed.

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(6) F. Feher, W. Kolb, and L. Leverenz, *Z. Naturforsch.*, **2a**, 454 (1947).

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In only a few cases have Raman spectra been obtained for these metal–ammine complexes because of their absorption at the blue mercury line (4358 Å) which is usually employed in excitation of the spectra. Terrasse, *et al.*,[15] have pointed out that Raman spectra are particularly useful in studying the metal–nitrogen vibrations. These vibrations give rise to such low intensities in the infrared spectra that incorrect assignments of metal–nitrogen stretching vibrations often have been made. These authors have observed Raman spectra of saturated aqueous solutions of hexaammine complexes of Rh(III) and Ni(II); and Poulet, Delorme, and Mathieu[16] have obtained Raman spectra of $[Pt(NH_3)_4]Cl_2$ and $[Pt(NH_3)_4Cl_2]Cl_2$. Haas and Hall have also noted the difficulties arising as a result of the low intensities of the metal–nitrogen stretching vibrations and have used He–Ne laser excitation to observe this vibrational frequency with $Co(NH_3)_6{}^{3+}$.[18] Raman spectra ascribed (probably incorrectly) to $Zn(NH_3)_6{}^{2+}$ and $Cd(NH_3)_6{}^{2+}$ were reported many years ago by Damaschun.[19]

In the following, we report Raman spectra for the ions $(H_3N)_2Ag^+$ and $(H_3N)_2Hg^{2+}$. Since there are certain discrepancies in the infrared spectra assigned to these cations in the literature, we also redetermined these. Both ions are colorless making it possible to use conventional excitation of the Raman spectra with a low-pressure mercury arc.

A normal-coordinate analysis was carried out using the same kind of force field (Urey–Bradley) for the isoelectronic sequences $(H_3N)_2Ag^+$, $(H_3C)_2Cd$, $(H_3C)_2Sn^{2+}$ and $(H_3N)_2Hg^{2+}$, $(H_3C)_2Hg$, $(H_3C)Tl^+$, $(H_3C)_2Pb^{2+}$. In addition, calculations were made for bis(trifluoromethyl)mercury to ascertain the effect on the mercury–carbon bond of altering the effective electronegativity of the carbon atom.

At the completion of this work, we became aware of similar calculations which had been made for $(H_3C)_2Cd$, $(H_3C)_2Hg$, and $(F_3C)_2Hg$.[20] The values of the force constants calculated for these three molecules are essentially the same as those reported in this work.

## Experimental Section

**Preparation of Compounds.**—Diamminemercury(II) bromide and chloride were prepared by treating $HgCl_2$ or $HgBr_2$ with excess liquid ammonia. After evaporation of the excess ammonia to dryness, the compounds were washed with ethanol and dried in a vacuum desiccator overnight. *Anal.* Calcd for $Hg(NH_3)_2Cl_2$: N, 9.1; Cl, 23.2. Found: N, 8.7; Cl, 23.0. Calcd for $Hg(NH_3)_2Br_2$: N, 7.1; Br, 40.5. Found: N, 7.0; Br, 43.4.

Solutions of diamminesilver(I) nitrate or perchlorate were prepared by dissolving a weighed quantity of reagent grade $AgNO_3$ or $AgClO_4$ in a solution containing 2 equiv of ammonia. The solid compounds were isolated by chilling a concentrated solution, collecting the crystals on a frit, and drying in a vacuum desiccator.

**Raman Spectra.**—The Raman spectra were excited with 4358-Å light from a Toronto arc and recorded photoelectrically with a Cary Model 81 Raman spectrophotometer which was calibrated with carbon tetrachloride and benzene. Recorded frequencies are accurate to within ±2 cm$^{-1}$ for strong, sharp bands.

The spectra for the diamminemercury(II) compounds were obtained with the solid compounds using hollow conical cells. The inside diameter of the cone was *ca.* 10 mm, the outside diameter was *ca.* 18 mm, and *ca.* 2 g of compound was required to fill the cell. Spectra were also recorded for Nujol mulls, and no shifts were observed in the frequencies determined. The cell used for these mull spectra consisted of a glass cone with a base *ca.* 10 mm in diameter. Light was scattered from this open end into the spectrophotometer. The compound was mixed with the mulling agent and applied evenly to the inside of the cone using a second conical piece of glass made to fit the outer cone with a clearance of approximately 1 mm. Spectra of the diamminesilver ion were recorded with aqueous solutions. The general experimental procedures were similar to those described earlier.[21] Attempts to obtain Raman spectra with powder and mull samples of $[(H_3N)_2Ag]ClO_4$ or $[(H_3N)_2Ag]NO_3$ led to photolysis of the compound and a very high background caused by the scattering from the metallic silver. The spectra of the diamminesilver(I) solutions as well as the spectrum of aqueous ammonia were obtained while maintaining the solutions at *ca.* 0° by pumping water through a jacket around the Raman cell.

**Infrared Spectra.**—The infrared spectra were recorded with a Perkin-Elmer Model 521 grating spectrometer calibrated with polystyrene film. All data were obtained using the split-mull technique and the solid compounds. Cesium iodide windows were used throughout.

## Results

**Assignment of the Spectra of the Ammine Complexes. Diamminesilver(I) Complexes.**—The Raman spectrum of aqueous $(H_3N)_2Ag^+NO_3^-$ is illustrated in Figure 1 and the infrared spectrum of a mull of the solid compound is shown in Figure 2. As can be seen from Figure 2, it was not possible to obtain a high-quality infrared spectrum of this compound. Values for both diamminesilver(I) nitrate and perchlorate are tabulated in Table I.

The infrared spectrum of $(H_3N)_2Ag^+$ has been obtained previously with the crystalline sulfate salt.[22,23] The agreement between the spectra of the sulfate and the perchlorate and nitrate salts studied in this work is good, the only significant difference being the value of the ammine rocking frequency which is 100 cm$^{-1}$ higher in the sulfate spectra.

There is no clear feature in the infrared spectrum which can be assigned to the antisymmetric N–Ag–N stretching fundamental, although there is a very broad band (width at half-height *ca.* 50 cm$^{-1}$) at about 430 cm$^{-1}$ which we have assigned, with some hesitation, to this vibration. In the Raman spectrum of the solutions of the nitrate and perchlorate, a strong line, surely assignable to the symmetric N–Ag–N stretching mode, is observed at *ca.* 370 cm$^{-1}$ and, surprisingly, is only very weakly polarized. With the exception of these two difficulties, the assignments are made easily by comparison with the isoelectronic dimethyl compounds, on the basis of the Raman polarizations, and using the results of previous studies of ammine complexes. These assignments are collected in Table I.

Both the Raman and infrared spectra show three vi-

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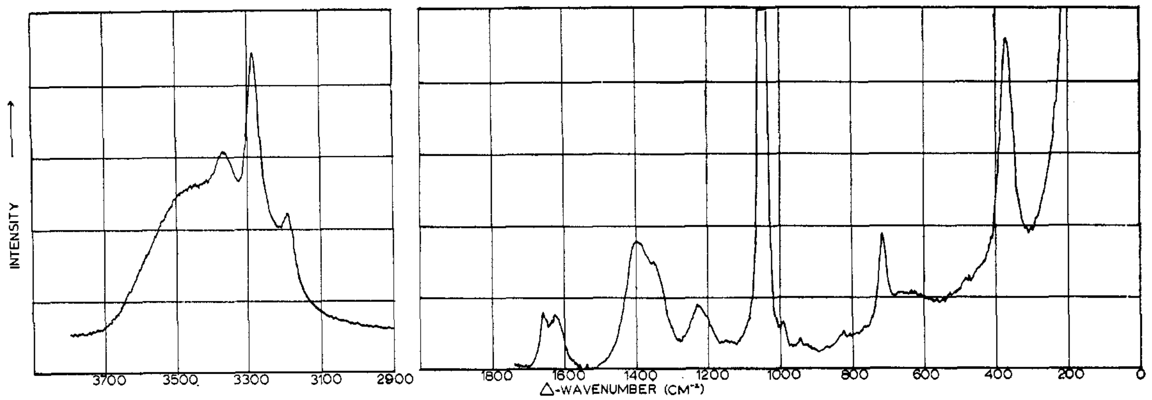

Figure 1.—Raman spectrum of aqueous $[(H_3N)_2Ag]NO_3$.

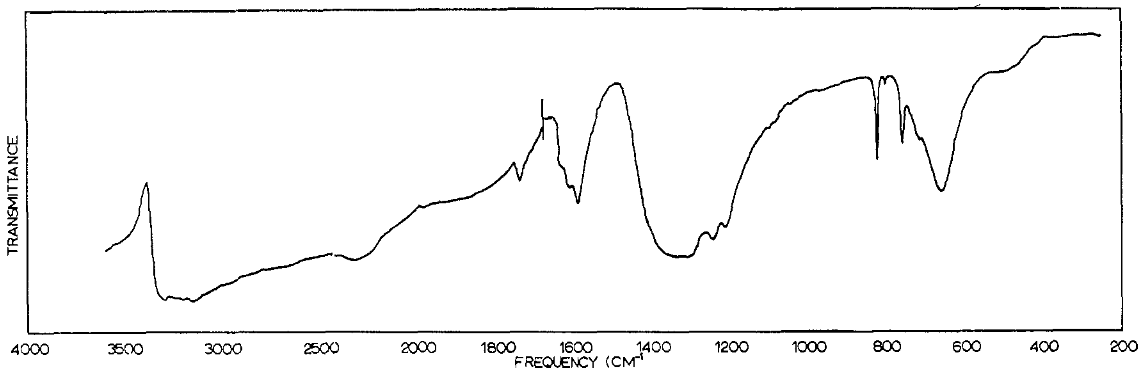

Figure 2.—Infrared spectrum of $[(H_3N)_2Ag]NO_3$.

TABLE I

OBSERVED FREQUENCIES OF DIAMMINESILVER(I) COMPLEXES

| Raman | | | Infrared | | | | |
|---|---|---|---|---|---|---|---|
| $[(H_3N)_2Ag]ClO_4$,[a] satd aq soln, cm$^{-1}$ | $[(H_3N)_2Ag]NO_3$,[b] satd aq soln, cm$^{-1}$ | Assignment | $[(H_3N)_2Ag]ClO_4$,[c] mull, cm$^{-1}$ | $[(H_3N)_2Ag]NO_3$,[d] mull, cm$^{-1}$ | $[(H_3N)_2Ag]_2SO_4$,[f] cm$^{-1}$ | $[(H_3N)_2Ag]_2SO_4$,[g] cm$^{-1}$ | Assignment |
| [e] | 3373 dp | $\nu(NH_3)_{asym}$ | 3360 | | 3290 | 3330 | $\nu(NH_3)_{asym}$ |
| 3293 | 3287 p | $\nu(NH_3)_{sym}$ | 3290 | 3305 | 3230 | 3250 | $\nu(NH_3)_{sym}$ |
| 3203 | 3195 p | $2\delta(NH_3)_{deg}$ | 3185 | 3155 | 3140 | 3140 | $2\delta(NH_3)_{deg}$ |
| 1658 | 1658 p | $\delta(NH_3)_{deg}$ | 1625 | 1632 | 1640 | 1650 | $\delta(NH_3)_{deg}$ |
| 1634 | 1624 | | 1610 | 1618 | | | |
| | | | | | 1600 | | |
| | | | | 1590 | | | |
| 1223 | 1224 p | $\delta(NH_3)_{sym}$ | 1244 | 1238 | | | |
| | | | | | 1190 | 1215 | $\delta(NH_3)_{sym}$ |
| | | | 1206 | 1209 | | | |
| | | | 650 | 656 | 741 | 738 | $\rho(NH_3)_{rock}$ |
| 369 | 372 (p?) | $\nu(AgN_2)_{sym}$ | ~430 (?vvb) | ~430 (?vvb) | | | $\nu(AgN_2)_{asym}$ |

[a] Perchlorate lines are observed at 1107 ($\nu_3$), 934 ($\nu_1$), 629 ($\nu_4$), and 460 ($\nu_2$) cm$^{-1}$. [b] Nitrate lines are observed at 1399 ($\nu_3$), 1048 ($\nu_1$), and 715 ($\nu_4$) cm$^{-1}$. [c] Perchlorate bands are observed at 1090 ($\nu_3$), 940 ($\nu_1$), 626 ($\nu_4$), and 432 ($\nu_2$) cm$^{-1}$. [d] Nitrate bands are observed at 1400 ($\nu_3$) and 823 ($\nu_2$) cm$^{-1}$. [e] Masked by water scattering. [f] See ref 22. [g] See ref 23.

brations in the range 3100–3400 cm$^{-1}$, rather than the expected two. Since this occurs even with the solution spectra, it cannot be ascribed to a splitting of the degenerate ammine stretch by crystal field effects, the usual explanation when this has been observed in infrared spectra of crystalline samples. A concentrated aqueous solution of ammonia recorded at 0° shows three Raman lines in this region at 3400 (s, dp), 3313 (vs, p), and 3234 (m) cm$^{-1}$, together with two very weak lines at 1642 and 1109 cm$^{-1}$. The highest two frequencies correspond to the fundamentals observed with liquid ammonia, 3380 ($\nu_3$) and 3294 ($\nu_1$) cm$^{-1}$. Consequently, the lines at *ca.* 3200 cm$^{-1}$ in the spectra of both aqueous ammonia and the diamminesilver(I) complex are assigned to the first overtone of an antisymmetric ammine deformation. This overtone is also observed in both the infrared and the Raman spectra of gaseous ammonia (symmetry species $A_1 + E$).[24] The analogous overtone is found frequently with the methyl complexes of heavy metals.

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(24) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1945, p 294.

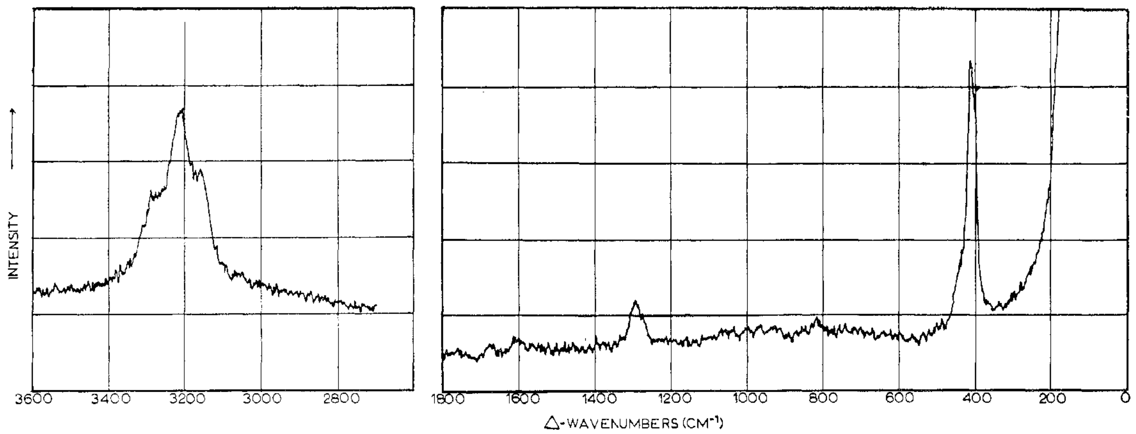

Figure 3.—Raman spectrum of crystalline $[(H_3N)_2Hg]Cl_2$.

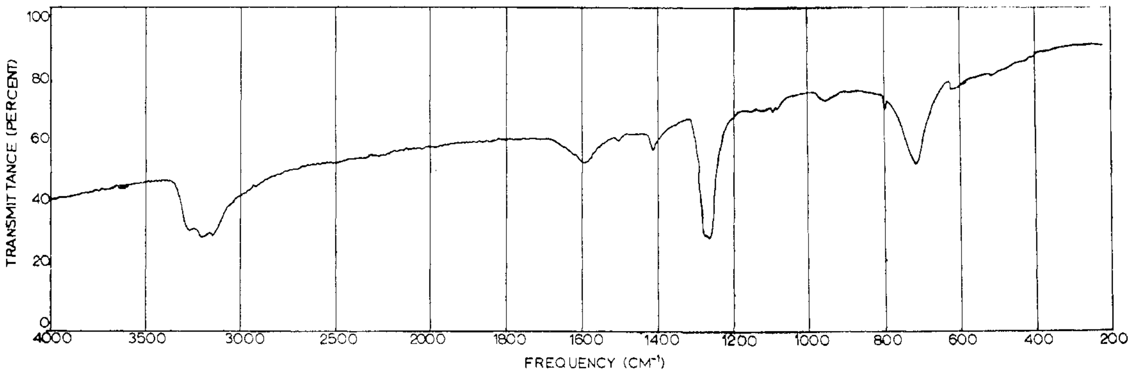

Figure 4.—Infrared spectrum of $[(H_3N)_2Hg]Cl_2$.

Table II

Observed Frequencies of Diamminemercury(II) Chloride

| Raman | | | Infrared | | | | |
|---|---|---|---|---|---|---|---|
| Powder,[a] cm⁻¹ | Mull, cm⁻¹ | Assignment | Mull,[a] cm⁻¹ | Ref 25, cm⁻¹ | Ref 26, cm⁻¹ | Ref 27, cm⁻¹ | Assignment |
| 3280 (5) | 3280 | $\nu(NH_3)_{asym}$ | 3265 (5) | | | | $\nu(NH_3)_{asym}$ |
| 3218 (10) | 3212 | $\nu(NH_3)_{sym}$ | 3197 (5) | | 3228 | | $\nu(NH_3)_{sym}$ |
| 3162 (5) | 3160 | $2\delta(NH_3)_{deg}$ | 3140 (5) | | 3118 | 3130 | $2\delta(NH_3)_{deg}$ |
| 1665 (0.25) | 1678 | $\delta(NH_3)_{deg}$ | | | | | $\delta(NH_3)_{deg}$ |
| 1610 (0.5) | 1605 | | 1595 (3) | 1597 | 1590 | 1605 | |
| 1293 (3) | 1289 | $\delta(NH_3)_{sym}$ | 1264 (10) | 1277<br>1264 | 1266 | 1270 | $\delta(NH_3)_{sym}$ |
| | | | 720 (7) | 720 | 720 | 719 | $\rho(NH_3)_{rock}$ |
| 412 (15) | 413 | $\nu(HgN_2)_{sym}$ | | | | 513 | $\nu(HgN_2)_{sym}$ |

[a] Relative intensities given in parentheses.

As expected, the vibrations of the nitrate and perchlorate anions in both the solution and crystal spectra are essentially those of the "free" anion.

**Diamminemercury(II) Complexes.**—The infrared spectrum of $(H_3N)_2Hg^{2+}$ has been studied by several authors.[6,25-27] The Raman and infrared spectra of $[(H_3N)_2Hg]Cl_2$ were obtained and are illustrated in Figures 3 and 4. Data for both the diamminemercury(II) chloride and bromide are tabulated in Tables II and III. Again three vibrations are observed in the range 3100–3300 cm$^{-1}$ in both the Raman and infrared spectra. In the literature, only the highest pair of frequencies, the lowest pair, or a broad structureless band has been reported for this region.

Again for the Hg–N stretching region, which has been of particular interest to several workers, differing results have been reported. Nakagawa and Shimanouchi[14] carried out a normal-coordinate analysis for $(H_3N)_2Hg^{2+}$ based on the data of ref 27 listed in Table II. For the antisymmetric N–Hg–N stretch, they used 513 cm$^{-1}$. Recently Clark[25] examined the region from 220 to 600 cm$^{-1}$ carefully using both $[(H_3N)_2Hg]Cl_2$ and $[(H_3N)_2Hg]Br_2$ and observed the very weak band at 513 cm$^{-1}$ only in the spectrum of the chloride. He questioned the assignment of this band to a fundamental. With complexes of the very heavy metals, both the M–C and the M–N vibrations give rise to very

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(25) R. J. H. Clark and C. S. Williams, *J. Chem. Soc., A*, 1425 (1966).

(26) K. Brodersen and H. J. Becker, *Chem. Ber.*, **89**, 1487 (1956).

(27) E. D. Bertin, I. Nakagawa, S. Mizushima, T. J. Lane, and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 525 (1958).

TABLE III

OBSERVED FREQUENCIES OF DIAMMINEMERCURY(II) BROMIDE

| Raman | | Infrared | | | | |
|---|---|---|---|---|---|---|
| Powder,[a] cm$^{-1}$ | Assignment | Mull,[a] cm$^{-1}$ | Ref 26, cm$^{-1}$ | Ref 25, cm$^{-1}$ | Ref 27, cm$^{-1}$ | Assignment |
| 3291 (5) | $\nu(NH_3)_{asym}$ | 3260 (5) | 3260 | | | $\nu(NH_3)_{asym}$ |
| 3209 (10) | $\nu(NH_3)_{sym}$ | 3193 (7) | 3160 | | | $\nu(NH_3)_{sym}$ |
| 3142 (5) | $2\delta(NH_3)_{deg}$ | 3120 (7) | | | | $2\delta(NH_3)_{deg}$ |
| 1668 (–)[b] | | | | | | |
| 1602 (–)[b] | $\delta(NH_3)_{deg}$ | 1584 | 1576 | 1595 | 1595 | $\delta(NH_3)_{deg}$ |
| | | 1397 (4) | | | | |
| 1263 (3) | $\delta(NH_3)_{sym}$ | 1237 (6) | 1240 | 1253<br>1240 | 1245 | $\delta(NH_3)_{sym}$ |
| | | 715 (4) | | | | |
| | | 680 (4) | 687 | 721<br>700 | 697 | $\rho(NH_3)_{rock}$ |
| 380 (15) | $\nu(HgN_2)_{sym}$ | | | | 499 | $\nu(HgN_2)_{asym}$ |

[a] Relative intensities given in parentheses. [b] Too weak to measure.

low intensities in the infrared spectra and often cannot be observed, although they are quite intense in the Raman effect. We could not with confidence make any assignment of a mercury–nitrogen stretch from our infrared spectra. The increase of 33 cm$^{-1}$ for the symmetric Hg–N stretch in going from the bromide to the chloride indicates some interaction between the mercury atom and the halide ions. In these complexes, the mercury atom is surrounded by four halide ions in the equatorial positions with the ammine groups in the axial positions.[28,29] By comparison, the corresponding vibration of the isoelectronic $(H_3C)_2Tl^+$ ion changes only from 488 cm$^{-1}$ in $(H_3C)_2TlBr$ to 493 cm$^{-1}$ in $(H_3C)_2TlCl$.[30]

It was not possible to obtain Raman spectra of $(H_3N)_2Hg^{2+}$ in aqueous solution because the complex decomposes in water and is only very slightly soluble in the presence of the high concentrations of $NH_4Cl$ required to prevent decomposition. Infrared spectra of $[(H_3N)_2Hg](NO_3)_2$ were also recorded, but strong hydrogen-bonding interactions in the crystal gave rise to very poor spectra. Some of the infrared spectra reported in the literature have been obtained using KBr disks.[24] We observed reactions whenever disks were prepared (perhaps with moisture) giving intense new bands at *ca.* 3530, 3480, 1601, and 1580 for both the chloride and bromide. Consequently, only data obtained with mulls were used in the subsequent calculations.

Trends in the frequencies of several isosteric ammine and methido complexes are illustrated in Figure 5.

**Force Constant Calculations.**—The molecular model of the $(X_3Y)_2Z$ ions and molecules used in the calculations is shown in Figure 6. The point group was taken as $D_{3d}$[31] and the representation of the normal vibrations is $3A_{1g} + A_{1u} + 3A_{2u} + 3E_g + 4E_u$. Figure 6 also shows the 22 internal coordinates used in the calculations. Torsional motion was ignored.

Table IV lists the molecular parameters used in constructing the *G* matrices.[14,28,29,32–40]

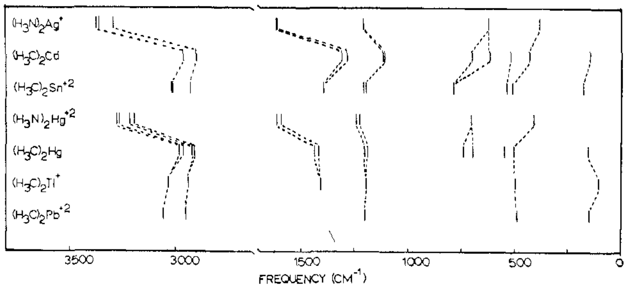

Figure 5.—Correlation of the vibrational frequencies of isoelectronic ammine and methide complexes.

A Urey–Bradley field (1) was used to express the

$$2V = \sum_{i=1}^{6} [2K'_{YX}r_{YX}(\Delta r_{YX}^i) + K_{YX}(\Delta r_{YX}^i)^2] + \sum_{i=1}^{2} [2K'_{YZ}R_{YZ}(\Delta R_{YZ}^i) + K_{YZ}(\Delta R_{YZ}^i)^2] + \sum_{i=1}^{6} [2H'_{\alpha}(\Delta\alpha^i) + H_{\alpha}(\Delta\alpha^i)^2] + \sum_{i=1}^{6} [2H'_{\beta}(\Delta\beta^i) + H_{\beta}(\Delta\beta^i)^2] + \sum_{i=1}^{2} [2H'_{YZY}(\Delta\phi_{YZY}^i) + H_{YZY}(\Delta\phi_{YZY}^i)^2] + \sum_{i=1}^{6} [2F'_{XX}q_{XX}(\Delta q_{XX}^i) + F_{XX}(\Delta q_{XX}^i)^2] + \sum_{i=1}^{6} [2F'_{XZ}q_{XZ}(\Delta q_{XZ}^i) + F_{XZ}(\Delta q_{XZ}^i)^2] \quad (1)$$

potential energy. After elimination of the nonbonded distances $q_{XX}$ and $q_{XZ}$, the potential energy expression contains all of the quadratic force constants in eq 1, the linear constants $F'_{ij}$, and the additional force constant $\kappa$ resulting from the redundancy in the six angles about the carbon or nitrogen atoms.[41] As is conventional, the linear term $F'$ is taken as $-0.1F$ assuming the repulsive energy to be proportional to $q^{-9}$.

The assumed starting values of the force constants were adjusted so as to minimize the sum of the squares of the residuals in the frequency parameters. Weights were proportional to $1/\lambda$. The calculations were carried out using standard computer programs[42–44] and the

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(29) W. Rudorff and K. Brodersen, *Z. Anorg. Allgem. Chem.*, **270**, 145 (1952).

(30) M. J. Sprague and R. S. Tobias, unpublished results.

(31) B. Kirtman, *J. Chem. Phys.*, **40**, 390 (1964).

(32) The value for $(CH_3)_4Sn$ is given as 2.17 Å: H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, **40**, 164 (1944). The Sn–C distance is probably somewhat shorter in the cation, and the value used was taken from $(CH_3)_2SnF_2$: E. O. Schlemper and W. C. Hamilton, *Inorg. Chem.*, **5**, 995 (1966). Calculations were also made with the longer distance, and no significant changes in force constants or frequencies were observed.

(33) A. H. Gregg, *Trans. Faraday Soc.*, **33**, 852 (1937).

(34) R. W. G. Wyckoff, "Crystal Structures," Vol. 4, Interscience Publishers, Inc., New York, N. Y., 1948, p 17.

(35) L. O. Brockway and H. O. Jenkins, *J. Am. Chem. Soc.*, **58**, 2936 (1936).

(36) R. B. Corey and R. W. G. Wyckoff, *Z. Krist.*, **87A**, 264 (1934).

(37) Reference 27 reports 2.03 Å for $[(H_3N)_2Hg]Cl_2$. We have taken 2.05 Å for comparison with Nakagawa and Shimanouchi's calculation.[14]

(38) Taken to match values by J. Overend and J. R. Scherer, *J. Opt. Soc. Am.*, **50**, 1203 (1960). Data from ref 32.

(39) Taken to match the values used by Nakagawa and Shimanouchi.[14]

(40) J. Sheridan and M. Gordy, *J. Chem. Phys.*, **20**, 591 (1952).

(41) The force constant, $\kappa$, the intramolecular tension, can be expressed in terms of the linear terms in the potential energy: T. Shimanouchi, *J. Chem. Phys.*, **17**, 245 (1949).

(42) E. Wu, Ph.D. Thesis, University of Minnesota, 1962.

(43) J. Overend and J. R. Scherer, *J. Chem. Phys.*, **32**, 289 (1960).

(44) J. R. Scherer and J. Overend, *ibid.*, **32**, 1720 (1960).

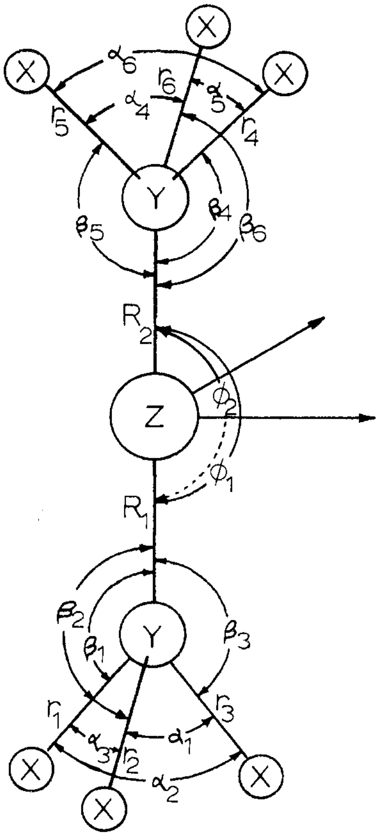

Figure 6.—Molecular model showing the internal coordinates used for the $(X_3Y)_2Z$ molecules and ions.

Table IV

Molecular Parameters[a]

| Parameter | Value, Å | Parameter | Value, Å |
|---|---|---|---|
| $R$(Cd–C) | 2.15[14] | $R$(Hg–N) | 2.11 (bromide)<br>2.05[28,29,37] (chloride) |
| $R$(Sn–C) | 2.08[32] | $r$(C-H) | 1.09[38] |
| $R$(Hg–C) | 2.23[33] | $r$(N-H) | 1.03[39] |
| $R$(Tl–C) | 2.01[34] | $r$(C–F) | 1.33[40] |
| $R$(Pb–C) | 2.30[35] | | |
| $R$(Ag–N) | 1.88[36] | | |

[a] ∠X–Y–X = ∠X–Y–Z = tetrahedral angle.

University of Minnesota's CDC-1604 or 6600 computer. The results are tabulated in Tables V–IX.

The starting values of the force constants $K$(CH), $H$(HCH), and $F$(H···H) were transferred from the tetramethyltin molecule[38] to the dimethyltin(IV) ion. The starting force constants $K$(SnC) and $H$(CSnC) were taken as those from the three-atom-model calculation using effective masses.[4] Different reasonable values of $H$(HCSn) and $F$(H···Sn) were then used in the least-squares refinement, and these converged to the same final values. The refined values obtained for $(CH_3)_2Sn^{2+}$ were then transferred together with the skeletal force constants estimated for the appropriate molecule or ion from the three-atom model to give zero-order values for the remaining dimethyls. In the case of the ions $(H_3C)_2Tl^+$ and $(H_3C)_2Pb^{2+}$, the number of observed frequencies was small, and so the force constants $H$(HCM) and $F$(H···M) were transferred from the isoelectronic $(H_3C)_2Hg$.

For the diamminemercury(II) ion, the zero-order values of $K$(NH), $H$(HNH), $H$(HMHg), $F$(H···H), and $F$(H···Hg) were estimated from earlier calculations on metal ammines,[23] and the skeletal force constants were transferred from dimethylmercury. Finally these constants after refinement were transferred for the zero-order calculation on $(H_3N)_2Ag^+$. The zero-order values for bis(trifluoromethyl)mercury were transferred from trifluoromethyl iodide[45] and from dimethylmercury.

In the calculations of the force constants for these $(X_3Y)_2Z$ ions and molecules, the skeletal stretching force constants $K$(YZ) and intramolecular tensions $\kappa$ were found to be ill determined. These two force constants are very highly correlated, and it was necessary to constrain only one to obtain a stable solution. With the methide complexes, it was found that the over-all frequency fit was but little changed as $\kappa$ was constrained in a refinement at values ranging from $+0.1$ to $-0.01$, so $\kappa$ was constrained at 0 in all of the calculations. This also permits comparisons with other calculations.[14] A strong correlation was also observed between the skeletal stretching force constant $K$(YZ) and the nonbonded interaction $F$(X···Z).

The force constant $H$(YZY) is determined almost exclusively by the frequency of the skeletal bending motion. The corresponding frequencies have been reported in the range 100–200 cm$^{-1}$, usually from Raman data where they often appear weakly as "forbidden"[31] transitions. In some cases, it has been difficult to distinguish them from the grating ghosts which appear frequently in this region. The values of these frequencies and consequently those of the force constants are doubtful in many cases. The potential energy distribution for the vibrations of $(H_3C)_2Sn^{2+}$ is given in Table IX and that for $(H_3N)_2Hg^{2+}$ is given in Table X; they are typical of these ions and molecules. The normal vibrational modes of $(H_3C)_2Sn^{2+}$ are illustrated in Figure 7. There is very little coupling between the skeletal vibrations and the ligand stretching and bending modes in any of the ammine or the simple methyl derivatives.

In the case of $(F_3C)_2Hg$, the least-squares regression analysis leads to a very large fluorine–fluorine nonbonding interaction constant and a small and negative constant for FCF bending. If the value of $F$(F···F) is constrained at 1.24 mdyn/Å as reported by Taylor[45] for $CF_3I$, the value of $H$(FCF) is then 0.53 mdyn Å/radian$^2$, similar to the value reported by Taylor for $CF_3I$, 0.456 mdyn Å/radian$^2$. At the same time, the mercury–carbon stretching force constant increases from 1.81 to 2.71 mdyn/Å. The average error in the frequency fit is only increased from 1.22 to 1.50% by this procedure. It, perhaps, should be noted that Taylor's force constants, while leading to very good agreement between observed and calculated frequencies, are not necessarily unique, and their calculation involved neglect of linear potential terms arising from the nonbonded interac-

(45) R. C. Taylor, *J. Chem. Phys.*, **22**, 714 (1954).

TABLE V

UBFF FORCE CONSTANTS[a,b]

| | Stretching | | Bending | | | | Repulsion | |
|---|---|---|---|---|---|---|---|---|
| Methide complexes | $K$(MC) | $K$(CH) | $H$(HCH) | $H$(HCM) | $H$(CMC) | | $F$(M···H) | $F$(H···H) |
| $(CH_3)_2Cd$ | 1.11 ± 0.23 | 4.51 ± 0.08 | 0.47 ± 0.03 | 0.00 ± 0.10 | 0.41 ± 0.10 | | 0.39 ± 0.13 | 0.09 ± 0.05 |
| $(CH_3)_2Sn^{2+}$ | 1.51 ± 0.02 | 4.69 ± 0.02 | 0.48 ± 0.01 | 0.12 ± 0.01 | 0.56 ± 0.02 | | 0.40 ± 0.02 | 0.05 ± 0.01 |
| $(CH_3)_2Hg$ | 1.25 ± 0.23 | 4.49 ± 0.08 | 0.50 ± 0.02 | −0.04 ± 0.13 | 0.53 ± 0.12 | | 0.52 ± 0.17 | 0.10 ± 0.04 |
| $(CH_3)_2Tl^{+}$ [b] | 1.15 ± 0.13 | 4.69 ± 0.11 | 0.51 ± 0.03 | −0.04[d] | 0.23 ± 0.08 | | 0.52[d] | 0.04 ± 0.07 |
| $(CH_3)_2Pb^{2+}$ [b,c] | 0.96 | 4.79 | 0.56 | −0.04[d] | 0.51 | | 0.52[d] | 0.02 |
| Amine complexes | $K$(MN) | $K$(NH) | $H$(HNH) | $H$(HNM) | $H$(NMN) | | $F$(M···H) | $F$(H···H) |
| $(NH_3)_2Ag^+$ | 0.31 ± 0.02 | 5.88 ± 0.02 | 0.600 ± 0.004 | −0.14 ± 0.005 | 0.3[e] | | 0.60 ± 0.02 | 0.064 ± 0.009 |
| $(NH_3)_2Hg^{2+}Cl^-$ | 0.85 ± 0.06 | 5.62 ± 0.06 | 0.57 ± 0.01 | 0.05 ± 0.02 | 0.3[e] | | 0.38 ± 0.06 | 0.08 ± 0.03 |
| $(NH_3)_2Hg^{2+}Br^-$ | 0.53 ± 0.07 | 5.62 ± 0.07 | 0.58 ± 0.02 | −0.02 ± 0.02 | 0.3[e] | | 0.44 ± 0.07 | 0.06 ± 0.03 |
| Bis(trifluoromethyl)-mercury | $K$(MC) | $K$(CF) | $H$(FCF). | $H$(FCM) | $H$(CMC) | | $F$(M···F) | $F$(F···F) |
| $(CF_3)_2Hg$[f] (1) | 1.81 ± 0.11 | 4.37 ± 0.04 | −0.14 ± 0.05 | 0.50 ± 0.05 | 0.5[e] | | 0.31 ± 0.04 | 2.15 ± 0.07 |
| (2) | 2.71 ± 0.05 | 4.11 ± 0.06 | 0.53 ± 0.03 | 0.73 ± 0.03 | 0.5[e] | | 0.10 ± 0.03 | 1.24 |

[a] $K$ and $F$ in mdyn/Å; $H$ ($\kappa$) in mdyn Å/radian². [b] The intramolecular tension was constrained at 0 in these calculations. [c] Error estimates could not be made for $(CH_3)_2Pb^{2+}$, since the number of frequencies experimentally determined was equal to the number of force constants calculated. [d] Constrained. [e] Skeletal bending frequency has not been observed; this constant was constrained. [f] (1) Six constants refined; (2) five constants refined. $F$(F···F) constrained at 1.24 mdyn/Å.

TABLE VI

DIAGONAL ELEMENTS[a] OF $F$ MATRIX FOR $(X_3Y)_2Z$ MOLECULES (MDYN/Å)

| | $F_{dia}$ (YZ) | $F_{dia}$ (XY) | $F_{dia}$ (XYZ) | $F_{dia}$ (XYX) | $F_{dia}$ (YZY) |
|---|---|---|---|---|---|
| $(CH_3)_2Cd$ | 2.09 | 4.77 | 0.32 | 0.51 | 0.41 |
| $(CH_3)_2Sn^{2+}$ | 2.51 | 4.91 | 0.43 | 0.51 | 0.56 |
| $(CH_3)_2Hg$ | 2.58 | 4.80 | 0.39 | 0.55 | 0.53 |
| $(CH_3)_2Tl^+$ | 2.43 | 4.96 | 0.36 | 0.53 | 0.23 |
| $(CH_3)_2Pb^{2+}$ | 2.30 | 5.01 | 0.40 | 0.57 | 0.51 |
| $(NH_3)_2Ag^+$ | 1.79 | 6.20 | 0.27 | 0.63 | 0.3[b] |
| $(NH_3)_2Hg^{2+}$ | | | | | |
| $Cl^-$ anion | 1.82 | 5.87 | 0.33 | 0.61 | 0.3[b] |
| $Br^-$ anion | 1.66 | 5.86 | 0.31 | 0.60 | 0.3[b] |
| $(CF_3)_2Hg$[c] | | | | | |
| (1) | 2.56 | 7.24 | 0.84 | 1.39 | ... |
| (2) | 2.96 | 5.73 | 0.84 | 1.40 | ... |

[a] These are the elements of the unsymmetrized $F$ matrix based on internal coordinates and were obtained by transformation from the symmetrized matrix after refinement. [b] Constrained; this is just $H$(NMN). [c] (1) Six constants refined; (2) five constants refined. $F$(F···F) constrained.

tions. The results of both of the calculations are given in the Tables IX and X.

## Discussion

The normal coordinates of these linear diammine and dimethido complexes are very similar. Examination of the normal coordinates of $(H_3C)_2Sn^{2+}$, Figure 7, shows that the methyl groups vibrate almost as single masses in the skeletal modes.

The skeletal stretching vibrations of the ammine complexes give very broad bands in both the infrared and the Raman spectra, and the Raman scattering arising from the symmetric skeletal vibration is only very weakly polarized. These effects which are not observed with the methyl derivatives are probably a consequence of hydrogen bonding between the coordinated ammine groups and the solvent cage in solution or the surrounding anions in the crystal. Consequently the real vibrational mode will not be precisely described by these calculations. This effect is also probably similar to that observed for the vibrations of coordinated water molecules[12,21] and hydroxo groups[46] where coupling of the vibrations involving the ligand to those of the solvent molecules *via* hydrogen bonds also is to be expected.

The Urey–Bradley field generally gives a good fit to these molecules and ions. It does not reproduce the small splitting in the antisymmetric $X_3Y$ deformations $\nu_9$ and $\nu_{12}$ which have been observed with both the linear dimethyls and diammines. In these cases, the splittings are much smaller than those reported for diammineplatinum(II) complexes where they range from 60 to 140 cm⁻¹. In this latter case the splittings have been attributed to interaction of the ammine hydrogens with the d electrons. Such an interaction seems unlikely to be the cause of the effect with methyl groups. The poorest fit is obtained for the rocking frequencies of the dimethyl compounds where differences of $\nu_{10}$ from $\nu_{13}$ of 63 and 87 cm⁻¹ have been reported for $(H_3C)_2Cd$ and $(H_3C)_2Hg$, respectively. It would have been possible to modify the force field to fit these, but this did not seem justified in view of the diverse nature of the samples used in obtaining the spectra. The infrared data for $(H_3C)_2Cd$ and $(H_3C)_2Hg$ were obtained with the gaseous compounds. Raman spectra of $(H_3C)_2Hg$ and $(H_3C)_2Cd$ were obtained with neat liquids. The infrared spectrum of $(H_3C)_2Sn^{2+}$ was obtained with aqueous solutions as were the Raman spectra of $(H_3N)_2Ag^+$, $(H_3C)_2Sn^{2+}$, $(H_3C)_2Tl^+$, $(H_3C)_2Pb^{2+}$, and $(F_3C)_2Hg$. The average of values for the infrared band frequencies for solid $(F_3C)_2Hg$ and a benzene solution was used in the calculations. The Raman and infrared data for $(H_3N)_2Hg^{2+}$ were obtained with the crystalline compound as was the infrared spectrum of $(H_3N)_2Ag^+$.

The number of frequencies was the same as the number of force constants calculated for $(H_3C)_2Pb^{2+}$, so the calculation does not afford a check on the validity of the force field. The number of observed frequencies was

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(46) R. S. Tobias and S. Hutcheson, *J. Organometal. Chem.* (Amsterdam), **6**, 535 (1966).

TABLE VII

OBSERVED AND CALCULATED FREQUENCIES (CM$^{-1}$)[a]

| Methide complexes | $\nu_8(E_g)$ $\nu_{11}(E_u)$ $\nu(CH_3)_{asym}$ | $\nu_1(A_{1g})$ $\nu_5(A_{2u})$ $\nu(CH_3)_{sym}$ | $\nu_9(E_g)$ $\nu_{12}(E_u)$ $\delta(CH_3)_{deg}$ | $\nu_2(A_{1g})$ $\nu_6(A_{2u})$ $\delta(CH_3)_{sym}$ | $\nu_{10}(E_g)$ $\nu_{13}(E_u)$ $\rho(CH_3)_{rock}$ | $\nu_7(A_{2u})$ $\nu(MC)_{asym}$ | $\nu_3(A_{1g})$ $\nu(MC)_{sym}$ | $\nu_{14}(E_u)$ $\delta(CMC)$ | Av error, % |
|---|---|---|---|---|---|---|---|---|---|
| $(CH_3)_2Cd$ calcd | 2963 | 2904 | 1409 | 1134 1135 | 669 674 | 531 | 472 | 151 | 1.76 |
| Neat, obsd | 2963 ... | 2904 ... | 1384 1435 | 1129 1140 | 642 705 | 538 | 465 | 150 | |
| $(CH_3)_2Sn^{2+}$ calcd | 3017 3018 | 2934 | 1402 1403 | 1214 | 783 790 | 586 | 524 | 180 | 0.27 |
| Aq $ClO_4^-$ obsd | 3020 3015 | 2933 2935 | ... 1403 | 1226 1202 | ... 790 | 582 | 529 | 180 | |
| $(CH_3)_2Hg$ calcd | 2972 2973 | 2917 | 1459 | 1192 1194 | 738 742 | 551 | 514 | 150 | 1.62 |
| Neat obsd | 2965 2980 | 2910 2924 | 1443 1475 | 1182 1205 | 700 787 | 550 | 515 | 156 | |
| $(CH_3)_2Tl^+$ calcd | 3032 | 2941 | 1429 1430 | 1159 1161 | 720 717 | 534 | 499 | 114 | 0.54 |
| Aq $NO_3^-$, $ClO_4^-$ obsd | 3033 ... | 2939 ... | 1420 ... | 1195 ... | ... ... | ... | 498 | 114 | |
| $(CH_3)_2Pb^{2+}$ calcd | 3035 | 2951 | 1487 | 1208 1210 | 745 758 | 513 | 480 | 150 | 0 |
| Aq $ClO_4^-$ obsd | 3055 ... | 2951 ... | ... ... | 1208 ... | ... | ... | 480 | 150 | |
| Ammine complexes | $\nu(NH_3)_{asym}$ | $\nu(NH_3)_{sym}$ | $\delta(NH_3)_{deg}$ | $\delta$ $NH_3)_{sym}$ | $\rho(NH_3)_{rock}$ | $\nu(MN)_{asym}$ | $\nu(MN)_{sym}$ | $\delta(NMN)$ | Av error, % |
| $(NH_3)_2Ag^+$ calcd | 3366 3366 | 3290 3290 | 1639 1639 | 1227 1222 | 653 648 | 423 | 370 | ... | 0.16 |
| Aq $ClO_4^-$ obsd | 3373 3360 | 3290 | 1644 1635 | 1224 | 653 | ... | 370 | ... | |
| $(NH_3)_2Hg^{2+}$ calcd | | | | | | | | | |
| $Cl^-$ | 3272 3272 | 3206 3206 | 1617 1617 | 1277 1218 | 720 | 445 | 412 | ... | 0.62 |
| $Br^-$ | 3275 3275 | 3201 3201 | 1609 1609 | 1250 1251 | 698 | 411 | 380 | | 0.74 |
| $Cl^-$ anion obsd | 3280 3265 | 3215 3197 | 1640 1595 | 1291 1264 | 720 | ... | 412 | ... | |
| $Br^-$ anion obsd | 3291 3260 | 3209 3193 | 1635 1584 | 1263 1237 | 698 | ... | 380 | ... | |
| | $\nu(CF_3)_{asym}$ | $\nu(CF_3)_{sym}$ | $\delta(CF_3)_{deg}$ | $\delta(CF_3)_{sym}$ | $\rho(CF_3)_{rock}$ | $\nu(MC)_{asym}$ | $\nu(MC)_{sym}$ | $\delta(CMC)$ | Av error, % |
| $(CF_3)_2Hg$ calcd | | | | | | | | | |
| (1) | 1150 1150 | 1063 1064 | 521 521 | 710 718 | 257 265 | 279 | 217 | ... | 1.22 |
| (2) | 1151 1151 | 1051 1056 | 519 519 | 733 739 | 255 263 | 279 | 217 | ... | 1.50 |
| $(CF_3)_2Hg$ obsd | 1160 1140 | 1052 1075 | 515 526 | 713 715 | 261 262 | 274 | 226 | ... | |

[a] The frequency numbering scheme and qualitative descriptions of the modes are those given in ref 11.

TABLE VIII

PER CENT POTENTIAL ENERGY DISTRIBUTION FOR $(H_3C)_2Sn^{2+}$ [a]

| | Frequency, cm$^{-1}$ | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 3020 | 3015 | 2935 | 2933 | 1403 | 1226 | 1202 | 790 | 582 | 529 | 180 |
| $K(CH)$ | 96 | 96 | 94 | 94 | ... | ... | ... | 1 | 1 | 1 | ... |
| $K(CSn)$ | ... | ... | ... | ... | ... | 2 | 2 | ... | 66 | 66 | ... |
| $H(HCH)$ | ... | ... | ... | ... | 91 | 55 | 55 | 3 | 2 | 2 | ... |
| $H(HCSn)$ | ... | ... | ... | ... | 1 | 13 | 13 | 25 | ... | ... | ... |
| $H(CSnC)$ | ... | ... | ... | ... | ... | ... | ... | 1 | ... | ... | 99 |
| $F(H\cdots Sn)$ | ... | ... | 3 | 3 | 2 | 26 | 27 | 70 | 30 | 31 | ... |
| $F(H\cdots H)$ | 3 | 3 | 3 | 3 | 5 | 3 | 3 | ... | ... | ... | ... |

[a] Entries are rounded to the nearest per cent.

TABLE IX

PER CENT POTENTIAL ENERGY DISTRIBUTION FOR $[(H_3N)_2Hg]Cl_2$

| | Frequency, cm$^{-1}$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 3280 | 3265 | 3215 | 3197 | 1640 | 1595 | 1291 | 1264 | 720 | 412 |
| $K(NH)$ | 97 | 97 | 94 | 94 | ... | ... | ... | ... | 1 | 1 |
| $K(NHg)$ | ... | ... | ... | ... | ... | ... | 1 | 1 | ... | 54 |
| $H(HNH)$ | ... | ... | ... | ... | 93 | 93 | 66 | 66 | 2 | 4 |
| $H(HNHg)$ | ... | ... | ... | ... | ... | ... | 6 | 6 | 15 | ... |
| $H(NHgN)$ | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| $F(H\cdots Hg)$ | 2 | 2 | 2 | 2 | 1 | 1 | 24 | 24 | 82 | 41 |
| $F(H\cdots H)$ | 1 | 1 | 3 | 3 | 5 | 5 | 4 | 4 | ... | ... |

also limited for $(H_3C)_2Tl^+$. The values calculated for the methyl rocking frequencies, 717 and 729 cm$^{-1}$, are much higher than the value of 569 cm$^{-1}$ originally assigned from Raman spectra[16] and closer to the recently reported values from infrared studies (mulls) on $(H_3C)_2TlCl$ and $(H_3C)_2TlBr$,[47] 797 and 792 cm$^{-1}$, respectively. The value reported by these authors for the antisymmetric C–Tl–C frequency, 546 cm$^{-1}$, is also rather close to that calculated, 534 cm$^{-1}$, indicating that the Urey–Bradley field is fairly satisfactory for this ion.

The broad, weak band in the infrared spectrum of $(H_3N)_2HgCl_2$ at *ca.* 500 cm$^{-1}$ may be due to antisymmetric N–Hg–N stretching, since the calculated value is 472 cm$^{-1}$. With $(H_3N)_2Ag^+$ a similar broad, weak band is observed at *ca.* 430 cm$^{-1}$ while the calculated value is 399 cm$^{-1}$. Because of the uncertainty of these assignments, the experimental values were not used as input to the normal-coordinate calculations. Raman spectra prove to be much more reliable than infrared for studying the skeletal stretching vibrations of these heavy-metal complexes. Comparison with the previous normal coordinate analysis of the diamminemercury(II) ion[14] shows that the diagonal $F$ element obtained in this work for Hg–N stretching is about 25% smaller primarily because of the lower frequency used for the Hg–N stretching vibration. The Urey–Bradley constants are considerably different because the least-squares refinement seeks a solution with a relatively large $F(H\cdots Hg)$ and consequently a smaller force constant $K$(Hg–N).

With the dimethyls, the carbon–hydrogen stretching force constants and the corresponding diagonal elements of the $F$ matrix increase smoothly in an isoelectronic series as the atomic number of the central metal and hence as the species charge increases. The rather high values of these constants correlate qualitatively with the high values of the $^{13}C$–H spin–spin coupling constants observed for many of these heavy-metal methyls.[48] The metal–carbon stretching force constants and the diagonal elements of the $F$ matrix do show the expected increase from cadmium to tin, but they exhibit the reverse trend from mercury to lead as

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(47) W. Beck and E. Schuierer, *J. Organometal Chem.* (Amsterdam), **3**, 55 (1965).

(48) G. E. Glass, Ph.D. Thesis, University of Minnesota, 1967.

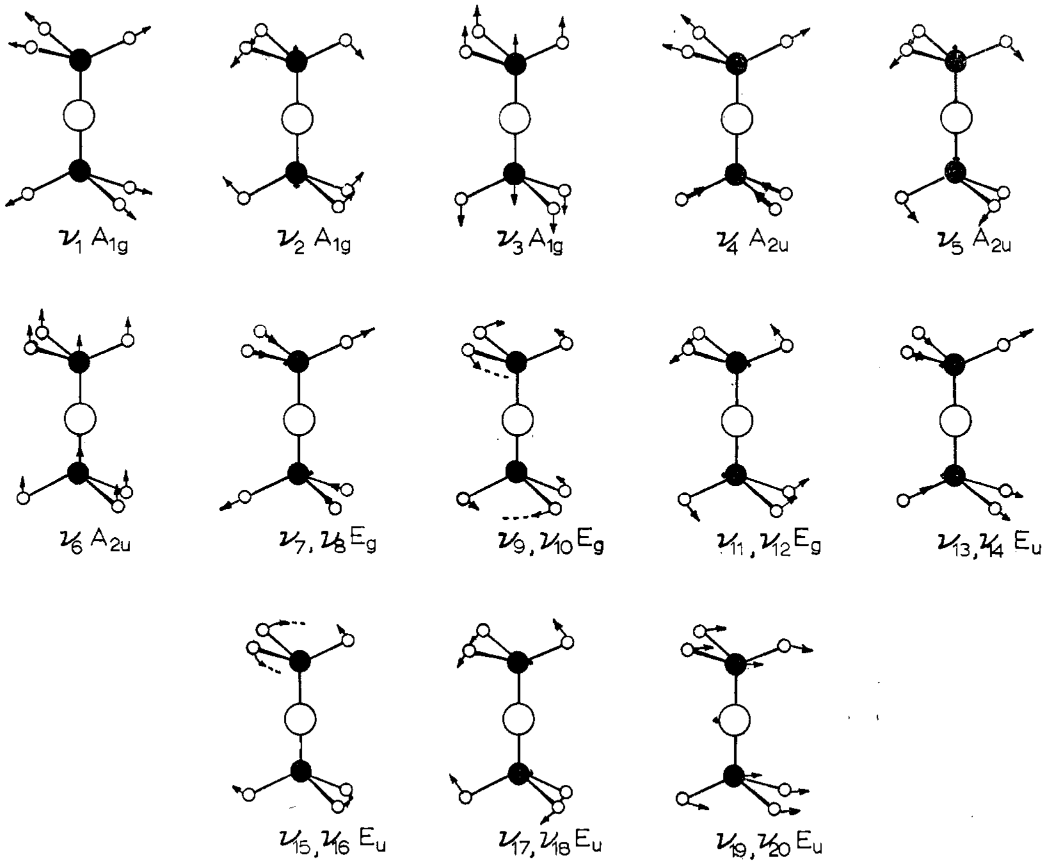

Figure 7.—Normal vibrational modes of the $(H_3C)_2Sn^{2+}$ ion.

first noted by Goggin.[49] For isosteric ammine and methyl complexes, there is a considerably greater resistance to the stretching of a metal–carbon than a metal–nitrogen bond.

The observed decrease in frequency and force constant for Hg–N stretching on going from $[(H_3N)_2Hg]Cl_2$ to $[(H_3N)_2Hg]Br_2$ correlates with the observed increase in the Hg–N bond length from 2.03 to 2.11 Å.

As is to be expected, the separation into skeletal vibrations and internal vibrations of the ligand is much less clear in the case of bis(trifluoromethyl)mercury than for the other molecules and ions studied. The solution sought by the least-squares analysis appears to be somewhat artificial in that the potential energy distribution shows that the nonbonded interactions dominate several of the calculated normal vibrations. The refinement with the fluorine–fluorine interaction constant constrained at the value from methyl iodide appears to give a more reasonable potential energy distribution. Since the diagonal $F$ elements for Hg–C stretching are about the same for the best fits of the $(H_3C)_2Hg$ and $(F_3C)_2Hg$ data, it seems unlikely that any extensive interaction of mercury d orbitals with $F_3C$ antibonding orbitals occurs.[50] However, since this constant depends to some extent upon the value of the nonbonded fluorine–fluorine interaction term, a small effect cannot be excluded.

**Acknowledgments.**—We wish to acknowledge the assistance of Mrs. Charlotte Smith throughout the computer calculations.

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[49] P. L. Goggin, Ph.D. Thesis, Oxford University, 1960.

[50] F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, **4**, 490 (1965).